

# Ultracold Li + Li<sub>2</sub> collisions: bosonic and fermionic cases

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We have carried out quantum dynamical calculations of vibrational quenching in Li + Li<sub>2</sub> collisions for both bosonic <sup>7</sup>Li and fermionic <sup>6</sup>Li. These are the first ever such calculations involving fermionic atoms. We find that for the low initial vibrational states considered here ( $v \leq 3$ ), the quenching rates are *not* suppressed for fermionic atoms. This contrasts with the situation found experimentally for molecules formed via Feshbach resonances in very high vibrational states.

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There is at present great interest in the properties of cold and ultracold molecules. At the end of 2003, three groups [1, 2, 3] created long-lived molecular Bose-Einstein condensates (BECs) from ultracold atomic gases by making use of magnetically tunable Feshbach resonances. The molecules are formed in highly excited vibrational states, and any vibrational relaxation will result in trap loss. A crucial breakthrough was the use of fermionic isotopes of the atomic gases (<sup>6</sup>Li, <sup>40</sup>K) tuned to large positive scattering lengths; it was found that in this case the atom-molecule and molecule-molecule inelastic collisions are strongly suppressed [4, 5, 6, 7], and the molecular cloud consisting of weakly bound dimers of fermions exhibits a remarkable stability against collisional decay. By contrast, for weakly bound dimers of bosonic atoms the vibrational relaxation is fast, so that the corresponding molecular cloud decays quickly and quantum degeneracy can be achieved only transiently [8, 9, 10, 11, 12]. Petrov *et al.* [13] have explained the important difference between molecular gases of weakly bound dimers formed from bosonic and fermionic atoms in terms of different quantum statistics for the atoms.

In this Letter, we carry out the first full quantum dynamics calculations for spin-polarized collisions of ultracold homonuclear molecules for Li + Li<sub>2</sub> in both the bosonic (<sup>7</sup>Li) and fermionic (<sup>6</sup>Li) cases. We find that for low-lying vibrational states there is no systematic suppression of the vibrational relaxation (quenching) rates for fermions, even when the scattering length is large and positive. The analysis of Petrov *et al.* [13] applies only when the scattering length is large and positive *and* the molecules are in their highest-lying vibrational state.

Quantum scattering calculations require accurate potential energy surfaces. We have previously shown that the interaction potential for spin-polarized (quartet) Li + Li<sub>2</sub> is highly non-additive [15], with a well depth 4 times that of the sum of Li-Li pair potentials. In the present work, we use a global Li<sub>3</sub> potential obtained from all-electron coupled-cluster electronic structure calculations,

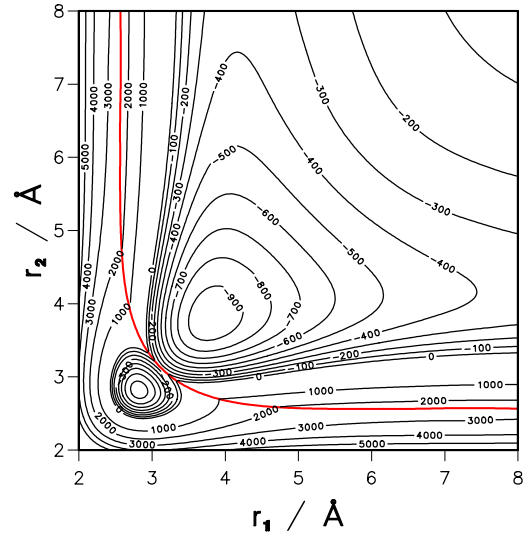


FIG. 1: Cut through Li<sub>3</sub> quartet surface at collinear geometries, showing seam between <sup>4</sup>Σ and <sup>4</sup>Π states. Contours are labelled in cm<sup>-1</sup>. The two minima are at depths of 760 and 950 cm<sup>-1</sup>.

which will be described in detail elsewhere [16]. In parallel work, Colavecchia *et al.* [17] have obtained another potential surface based on pseudopotential calculations. However, we chose to use our own surface in the present work because it takes better account of some features of the potential. In particular, as pointed out in Ref. 15, there is a seam of conical intersections at collinear geometries, between the <sup>4</sup>Σ surface that is the ground state at long range and a <sup>4</sup>Π surface that becomes the ground state inside  $r_1 = r_2 = 3.1$  Å. The resulting cusp drops to energies just below the atom-diatom threshold, as shown in Fig. 1, so may play a significant role in the dynamics. Our potential takes better account of this seam than that of ref. 17.

The methods we use to carry out quantum dynamics calculations on systems of this type have been described

in our previous work on  $\text{Na} + \text{Na}_2$  [18, 19] and elsewhere in the context of thermal reactive scattering [20], so a brief summary will suffice here. The potential energy surface is barrierless, so that it is essential to take reactive (atom exchange) collisions into account. The positions of the nuclei are described in hyperspherical democratic coordinates. The configuration space is divided into inner and outer regions, and the boundary between them is placed at a distance such that couplings due to the residual atom-diatom interaction can be neglected outside the boundary. In the inner region (hyperradius  $\rho \leq 45 a_0$  in the present case), we obtain the wavefunction for nuclear motion by propagating a set of coupled equations in a diabatic-by-sector basis that is obtained by diagonalizing a fixed- $\rho$  reference Hamiltonian in a basis set of pseudohyperspherical harmonics. In the outer region, we use the Arthurs-Dalgarno formalism [21], which is based on Jacobi coordinates, and compute by inwards integration regular and irregular solutions of a radial Schrödinger equation which includes the isotropic ( $R^{-6}$ ) part of the interaction. Matching between wavefunctions in the inner and outer regions yields the scattering S-matrix.

The difference between the  $^6\text{Li}$  and  $^7\text{Li}$  cases is implemented by selecting the pseudohyperspherical harmonic basis functions included in the basis set. For both bosons and fermions, we consider spin-stretched states of all three atoms involved (states with  $|M_F| = F = F_{\text{max}}$ ). For such states the nuclear spin wavefunction is symmetric with respect to any exchange of nuclei. However, the electronic wavefunction for the quartet state is antisymmetric with respect to exchange of nuclei. Thus, to satisfy the Pauli Principle, the wavefunction for nuclear motion must be antisymmetric with respect to exchange of bosonic nuclei (for fermionic alkali metal atoms) and symmetric with respect to exchange of fermionic nuclei (for bosonic alkali metal atoms).

Asymptotically, the hyperspherical functions correlate with atom-diatom functions; the diatom functions for Hund's case (b), which is appropriate for  $\text{Li}_2$  ( $^3\Sigma_u^+$ ), are labelled with a vibrational quantum number  $v$  and a mechanical rotational quantum number  $n$ ;  $n$  couples with the diatomic electron spin  $s = 1$  to give a resultant  $j$ , but for  $\text{Li}_2$  the splittings between states of the same  $n$  but different  $j$  are very small and are neglected here. In the  $^3\Sigma_u^+$  state, only even  $n$  is allowed for  $^7\text{Li}_2$  and only odd  $n$  for  $^6\text{Li}_2$ . In the outer region, we include rovibrational states with  $v = 0, 1, \dots, 7$  with all even rotational levels up to  $n_{\text{max}} = 32, 30, 28, 24, 22, 18, 14, 10$  for bosonic  $^7\text{Li}_2$  and rovibrational states with  $v = 0, 1, \dots, 7$  with all odd rotational levels up to  $n_{\text{max}} = 31, 27, 25, 23, 19, 17, 13, 7$  for fermionic  $^6\text{Li}_2$ . In the inner region, the number of coupled equations for bosonic atoms varies from 97 for total angular momentum  $J = 0$  to 827 for  $J = 10$  and for fermionic atoms it varies from 85 for  $J = 0^+$  to 782 for  $J = 11^-$ .

We have calculated the low-energy elastic and total

quenching cross sections  $\sigma(E)$  for  $^7\text{Li}_2$  colliding with  $^7\text{Li}$  and for  $^6\text{Li}_2$  colliding with  $^6\text{Li}$ , for bosons and fermions in all allowed initial states  $(v, n)$  with  $v \leq 3$  and  $n \leq 11$ . The cross sections for  $v = 1$  (with  $n = 0$  for  $^7\text{Li}_2$  and  $n = 1$  for  $^6\text{Li}_2$ ) are shown as a function of collision energy  $E$  in Figs. 2 and 3, together with the contributions from individual partial waves  $J$ . The partial wave sums are converged up to 500 mK for  $J_{\text{max}} = 10$ . For  $v = 1$ , both the elastic and inelastic cross sections are slightly smaller for  $^6\text{Li}$  than for  $^7\text{Li}$  at energies below 1 mK. However, the difference is only about a factor of 2, and it is *not* due to the difference between boson and fermion symmetries: for other values of  $v$  and  $n$  the ratio is often reversed.

At very low energies (up to about 1 mK), the cross sections are dominated by collisions with orbital angular momentum  $l = 0$ , for which there are no centrifugal barriers. A consequence of the symmetry constraints is that total angular momentum  $J = 0$  has an  $l = 0$  channel for  $^7\text{Li} + ^7\text{Li}_2$  but not for  $^6\text{Li} + ^6\text{Li}_2$ ; in the latter case the lowest partial wave containing  $l = 0$  is  $J = 1^-$ , where the superscript indicates odd parity. For this reason, low-energy calculations on  $^6\text{Li}$  are significantly more expensive than those on  $^7\text{Li}$ .

For nearly all initial  $v$  and  $n$ , and for both bosons and fermions, the ratio of inelastic to elastic cross sections is greater than 30 at  $E = 1 \mu\text{K}$  and remains greater than 1 throughout the Wigner regime (i.e., up to about 1 mK). The only exceptions to this are for rotational quenching of the  $(v, n) = (0, 2)$  state for bosons (ratio 4.3 at 1  $\mu\text{K}$ ) and the  $(0, 3)$  state for fermions (ratio 7.5), for which there is only one inelastic channel with  $l = 0$ .

Scattering calculations for  $\text{Li} + \text{Li}_2$  are converged up to about  $10^{-4}$  K using just a single partial wave ( $J = 0$  for  $^7\text{Li}$  and  $J = 1^-$  for  $^6\text{Li}$ ). At higher energies, other partial waves start to contribute significantly. For  $^7\text{Li}$  the contributions decrease monotonically with  $J$  at low energies because of centrifugal barriers corresponding to  $l = J$  for  $n = 0$ . For  $^6\text{Li}$ , the situation is slightly different: each partial wave is made up of a “parity favored” block (with parity  $(-1)^J$ ) and a “parity unfavored” block; the former includes an  $n = 1$  channel with  $l = J - 1$ , while for the latter the lowest  $l$  is  $l = J$ .

At collision energies below the centrifugal barrier, the partial cross sections follow Wigner laws,  $\sigma_{\text{inel}}^l \sim E^{l-1/2}$ . Since  $k_{\text{inel}}(E) = v_{\text{coll}} \sigma_{\text{inel}}(E)$ , where  $v_{\text{coll}} = (2E/\mu)^{1/2}$  is the collision velocity and  $\mu$  is the atom-diatom reduced mass, the inelastic rate coefficient is independent of  $E$  at limitingly low energies. For initial  $v = 1$ , the results in Figs. 2 and 3 give calculated limiting values  $k_{\text{inel}} = 5.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for bosons and  $2.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for fermions.

At energies above the barrier height, the inelastic probabilities saturate at values close to 1 and the energy dependence in each partial wave is then governed by the prefactor  $E^{-1}$  that multiplies the S-matrix term in the expression for the cross section. At energies high enough

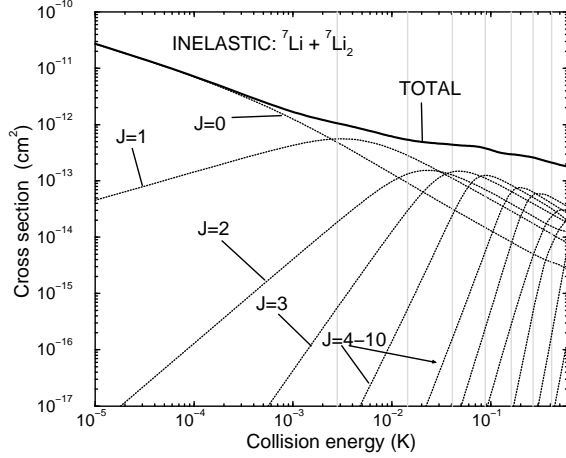
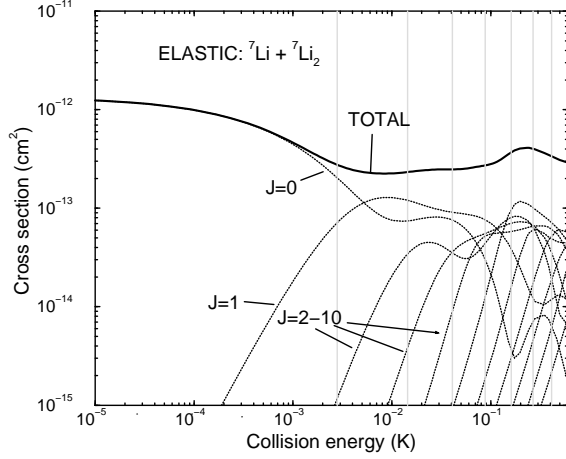


FIG. 2: Elastic cross sections (upper panel) and inelastic cross sections (lower panel) for  ${}^7\text{Li} + {}^7\text{Li}_2$  ( $v_i = 1$ ,  $n_i = 0$ ), with contributions from individual partial waves. The vertical lines indicate centrifugal barrier heights for  $l \geq 1$ .

that several partial waves (typically  $> 3$ ) contribute significantly to the overall cross sections, the energy dependence is described approximately by classical Langevin capture theory [22],

$$k_{\text{inel}}(E) = 3\pi(2E/\mu)^{1/2} \left( \frac{C_6}{4E} \right)^{1/3}, \quad (1)$$

where  $C_6 = 3086 E_h a_0^6$  is the isotropic atom-diatom dispersion coefficient. The Langevin result is compared with the full quantum results for the quenching rates for  $v = 1$  and 2 in Fig. 4; it may be seen that the Langevin and full quantum results agree semi-quantitatively at collision energies above about 10 mK for both bosons and fermions.

The atom-atom part of the potential used in our cal-

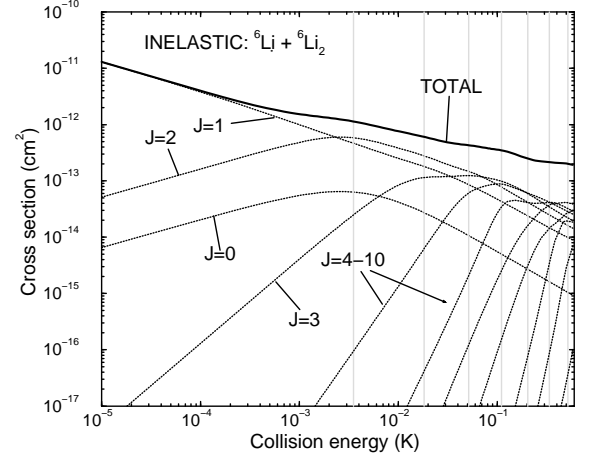
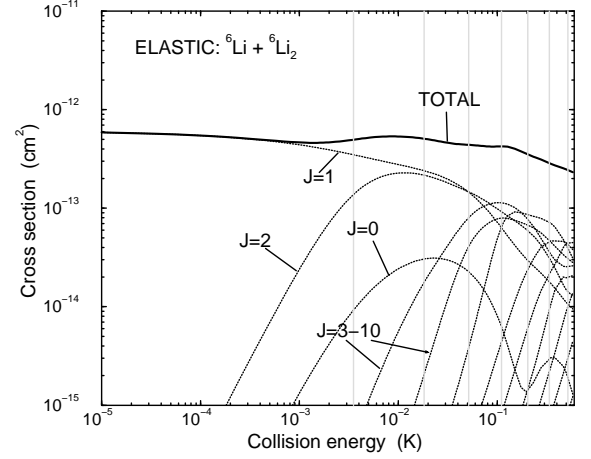


FIG. 3: Elastic cross sections (upper panel) and inelastic cross sections (lower panel) for  ${}^6\text{Li} + {}^6\text{Li}_2$  ( $v_i = 1$ ,  $n_i = 1$ ), with contributions from individual partial waves. The vertical lines indicate centrifugal barrier heights for  $l \geq 1$ .

culations gives triplet scattering lengths that are approximately correct for both  ${}^7\text{Li}$  ( $-26.35 a_0$ ) and  ${}^6\text{Li}$  ( $-1531 a_0$ ). However, at the magnetic field used in the molecule production experiments [1], the spin states involved had  $a \approx +3500 a_0$ , and it is important to establish whether fermionic suppression of quenching rates occurs for such large positive atom-atom scattering lengths. We have therefore repeated the calculations for energies  $E = 1 \mu\text{K}$  and 1 nK with the short-range part of the 2-body potential adjusted to reproduce  $a \approx 3500 a_0$ . (Slightly different adjustments were needed for bosons and fermions). Under these circumstances the calculated quenching rates for initial  $v = 1$  at limitingly low energy are  $7.7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  for  ${}^7\text{Li}$  and  $2.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for  ${}^6\text{Li}$ . This confirms that there is no fermionic suppression for the

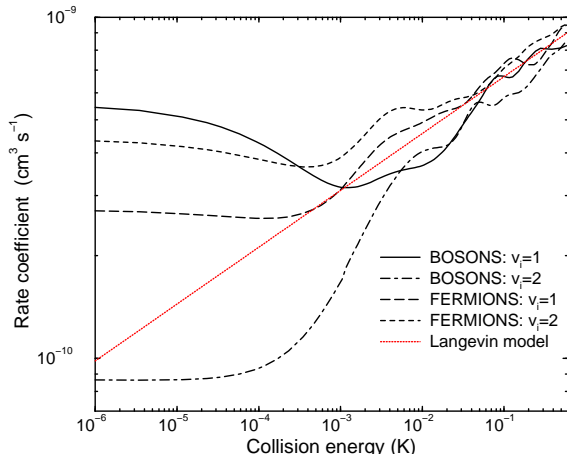


FIG. 4: Total inelastic rate coefficients for collisions of Li with Li<sub>2</sub> ( $v = 1$  and  $2$ , with  $n = 0$  for bosons and  $n = 1$  for fermions).

low-lying states that we consider.

The Langevin result, Eq. 1, may be used to predict inelastic rates for other atom-diatom alkali systems in spin-polarized states. Outside the Wigner regime, the inelastic rate coefficients for different systems will be proportional to  $C_6^{1/3}/\mu^{1/2}$ . The resulting inelastic rate coefficients for  $^{23}\text{Na}$ ,  $^{40}\text{K}$ ,  $^{87}\text{Rb}$  and  $^{133}\text{Cs}$  are lower than that for lithium by factors of 1.81, 1.75, 2.43, and 2.65, respectively, using  $C_6$  coefficients equal to twice the atomic dispersion coefficients from Ref. 23. The lower bound of applicability of the model may be estimated from the centrifugal barrier heights for  $l = 3$ , which are 6.86 mK, 1.89 mK, 0.537 mK, and 0.235 mK, for Na, K, Rb, Cs, respectively.

In conclusion, we have carried out full quantum dynamics calculations of vibrational relaxation (quenching) of  $^7\text{Li}_2$  by  $^7\text{Li}$  and of  $^6\text{Li}_2$  by  $^6\text{Li}$ , taking full account of the boson and fermion symmetries. We find that for low initial vibrational states of the molecules ( $v \leq 3$ ), there is *no* systematic suppression of the quenching rates for molecules formed from fermionic atoms, even when the atom-atom scattering length is large and positive. This contrasts with the situation for molecules formed in the highest vibrationally excited state [1, 2, 3].

Collisions of molecules involving *mixed* isotopes of-

fer fascinating new possibilities and in some cases allow identifiable chemical reactions even between ground-state molecules. For example, the reaction  $^7\text{Li} + ^6\text{Li}_2(v = 0) \rightarrow ^6\text{Li} + ^6\text{Li}^7\text{Li}(v = 0)$  is exothermic by 2.643 K because of the difference in zero-point energy of the two diatomic molecules. Calculations on collisions such as this will be described in future work.

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